

Quality Matters for Historical Plastics: The Past-Making of Cellulose Nitrates for Future Preservation

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Abstract

The material degradation of an historical artifact through chemical breakdown may place the object at the end of its useful heritage 'life' in terms of aesthetic value and appearance. But all is not lost in the ephemeral world of historical synthetic plastics. The chemical analyses of degraded cellulose nitrate artifacts have unlocked material clues that not only help explain stability variations to guide collection care and preservation, but also bring insight into past manufacturing materials, methods and quality control during production. Translating the industrial materials of a degrading artifact by understanding its past to inform its future can revive it with a new cultural significance, and engages heritage scientists, historians and conservators in an innovative community of "complementary science" as defined by Hasok Chang (2004).

Keywords: conservation science, modern plastic materials, cultural value, analytical chemistry, industrial heritage, history of science, cellulose nitrate, degradation, modern history.

Résumé

La dégradation matérielle d'un artefact historique par décomposition chimique peut amener l'objet à la fin de sa 'vie' patrimoniale utile en termes de sa valeur esthétique et son apparence. Néanmoins, tout n'est pas perdu dans le monde éphémère des plastiques synthétiques historiques. Les recherches en chimie analytique sur les artefacts en nitrate de cellulose dégradés ont révélé des indices matériels qui non seulement aident à expliquer les variations de stabilité pour améliorer la conservation mais engendrent aussi une connaissance accrue dans la fabrication des matériaux, les méthodes et contrôles de qualité lors de la production initiale. Décrypter le processus de dégradation de matériaux industriels en appréhendant son passé pour éclairer son avenir peut l'investir d'une signification culturelle nouvelle et implique les scientifiques qui se consacrent à la préservation du patrimoine, les historiens, et les restaurateurs dans une communauté originale que l'on peut qualifier de "sciences complémentaires" selon l'expression d'Hasok Chang (2004).

Mots-clés : science de la conservation, matériaux plastiques modernes, valeur culturelle, analyse chimique, patrimoine industriel, histoire des sciences, nitrate de cellulose, dégradation, histoire contemporaine.

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The creative science of taking a familiar material and chemically changing it into new forms is epitomized by the revolution in the industrial semi-synthesis of plastics from the mid-19th century onwards. The earliest embodiment was cellulose nitrate, known to many by its most familiar name Celluloid. Cellulose nitrate was made by chemical modification of the natural plant polymer, cellulose, and entered commercial production in the 1860's when synthetic organic chemistry and manufacturing technology were opening up new worlds of scientific possibilities for industry.

Historical examples of cellulose nitrate that have survived intact and in pristine condition to the present day are testimonies to the successful balance between raw materials, chemical processing and manufacturing skills. But what can be said of cellulose nitrate when the historical material degrades, as is happening to a small but nonetheless significant number of objects in heritage collections worldwide and exemplified by figure 1? Why are some cellulose nitrate artifacts succumbing to the effects of long-term aging more readily than others? As importantly, does chemical degradation mark the end-point of cultural heritage usefulness for such artifacts? These questions are important for conservation scientists and conservators to answer for the preservation of this landmark historical plastic.



Figure 1 - Two pictures of the same cellulose nitrate spectacle frames, in 2002 in visibly good condition (left) and in 2014 in a degraded state (right). (Source: Photographs courtesy of Yvonne Shashoua, National Museum of Denmark)

Degrading cellulose nitrate not only causes its own auto-catalytic destruction, but also releases corrosive volatile chemicals that can induce the breakdown of objects in its vicinity. Conservation research on cellulose nitrate degradation has focused mostly on analytical studies of chemical changes to the modified polymer, loss of its additive plasticizers, and the accelerating effects of increased temperature and relative humidity on its

breakdown (Reilly, 1991; Derrick *et al.*, 1993; Feller, 1994). This understanding has been invaluable for informed management of storage and display environments for historical cellulose nitrate plastic collections (The British Standard Institute, 2012, p. 21), but does not satisfactorily explain what triggers the seemingly random breakdown of the plastic in the first place.

In this essay, I will discuss how reconnecting the history of cellulose nitrate manufacture and the chemistry of past production with present-day material characteristics and chemical composition unveil a fuller picture that helps to explain the preservation behavior of this aged plastic. Within the books and journal articles published between the mid-19th century and mid-20th century about the making of cellulose nitrate, the technical details and chemistry of the process are well-described alongside practical issues that had to be overcome to produce a good-quality material. In these accounts we rediscover the importance of controlling the residual levels of a chemical in a fundamental stage of synthesis for the plastic. We find that the issue persisted from the earliest days of cellulose nitrate production until its industrial decline in the 1960s, and that quality affected the stability of the end-product even within its commercial lifetime. We also see that manufacturers used certain colorants and additives to stabilize the plastic by counteracting the effect of detrimental residues. Revisiting this information allows us to appreciate the material complexities of cellulose nitrate plastic which proved too unpredictable for manufacturers to manage – despite decades of dedicated research – when faced with competition from new petrochemical plastics.

By connecting the historical technical literature for the industrial production of cellulose nitrate plastic with its chemical composition in historical artifacts, we are able to generate a materially-focused body of primary evidence relating a product's quality to its long-term stability. Doing this enables us to re-contextualize the significance of a plastic artifact's materiality as it changes from an un-degraded to degraded state, in terms of its chemical value rather than its aesthetics or function. Thus the cultural value of the degraded heritage artifact takes on new meaning as a consequence of changes in its material composition. Instead of physical degradation marking the end-point in an artifact's usefulness to historical understanding, it becomes a new insight into less tangible aspects of industrial manufacture, such as the undocumented reasons and decisions made by the manufacturers about acceptable quality using technical and scientific know-how that we no longer know or appreciate. This raises two important ethical questions for de-acquisition of degraded historical materials. One is that we undervalue material change as an indicator of past manufacturing practice; if

the object is disposed of, the material evidence goes too. The other is that if the trigger for degradation is inherent in manufacture and in the material itself, and we do not appreciate that the trigger cannot be controlled or removed, then time, effort and resources are expended in a losing battle of preservation. Thus, more interdisciplinary dialogue is required among historians, conservation scientists, and conservators about the significance and value of such materials in a research context. Studying and evaluating our modern industrial material culture through this new perspective opens up a new community in history of science with many possibilities.

In this chapter, I discuss how the chemical challenges faced by cellulose nitrate plastic manufacturers in the past to assure quality control for their brand product has resulted in inherent properties affecting the preservation chances of the material as heritage artifacts. Addressing first the apparently random behavior of the aged plastic and its consequences for heritage collections, I show how documented manufacturing issues involving residual acids, additives, and the limited control of production variables that could not be overcome despite advances in chemical understanding, are linked. They reveal little change in material quality throughout a century of commercial manufacture. These are taken as material reference points to explain the chemical differences between degraded and un-degraded historical plastic examined at the bench of today's conservators and conservation scientists in a quest for strategies to preserve the material. The conclusion is that even if the material cannot be saved it acquires important new value and significance.

The Loss of Plasticity: From the Aging of Brand Materials to their Bench Analysis

- *Historical Context of an Interdisciplinary Project*

As a conservation scientist in a national museum who was surveying plastic artifacts across collections of decorative arts and technical and social history in the early 1990s (Quye, 1993), I, like my peers, was perplexed by the sudden unexpected breakdown of aged cellulose nitrate plastic. Indeed, most curators and conservators were used to regarding plastics as stable materials and of relatively little research value. In the 1980s, historical interest in the 19th century and early 20th century started to grow, and this is when people were surprised to find that 'everlasting' plastics could fall apart. Analysis of the degraded examples revealed cellulose nitrate to be a vulnerable plastic, along with cellulose acetate, poly(vinyl chloride), poly(urethanes) and synthetic rubber. When curators, conservators and heri-

tage scientists recognized the problem and became more observant, it was realized that certain plastics could degrade within six months even in good museum conditions (Keneghan, 2005). Surveys during the early 1990s of plastic artifacts in the Victoria and Albert Museum and British Museum revealed that 1% were a “high conservation” priority because they were actively degrading (Shashoua, 2009, p. 8-9). This number, although small, has a big impact because the vapors released from degrading cellulose nitrate affect not only the materials of the artifact itself but also other materials nearby. Cellulose nitrate was widely used to imitate relatively stable natural materials like ivory, mother of pearl and tortoiseshell, so it often goes unnoticed until a disguised artifact starts to behave unexpectedly by breaking down.

Most of these historical objects had entered the museum with an unknown user life behind them, yet despite a stable and controllable museum environment, something was causing a few to randomly fall apart even within sets of related objects manufactured at the same time by the same maker. In the late 1980s the degradation problems of historical cellulose nitrate plastic had just been recognized (Green & Bradley, 1988). Some conferences were organized on the subject, like “Saving the Twentieth Century: The Conservation of Modern Materials” held in 1991 in Ottawa (Grattan, 1993). Analytical studies by conservation scientists worldwide started reaching similar conclusions – the material was losing its flexibility-inducing plasticizers and the chemically-modified nitrocellulose polymer was breaking down (Shashoua & Ward, 1995). Yet these chemical changes could not explain satisfactorily the hit-or-miss behavior of the material. Amongst the many chemical complexities of this aged and aging historical plastic, might we be overlooking a basic inherent common factor linking the stability of today’s artifacts to past manufacturing processes?

With awareness rising amongst conservators and curators of unstable cellulose nitrate plastics in the late 1990s (Springate, 1997), the focus of explaining destabilization remained on the loss of nitrate from the cellulose. Some researchers suggested residual acids from manufacture as a possible reason (Selwitz, 1988; Reilly, 1991). Investigating this manufacturing residue as a cause of random breakdown in old cellulose nitrate required not only that the materials of the artifacts be studied, but also a better understanding of quality issues in past production. This would entail a different conservation science research approach, combining the polymer chemistry of historical plastics artifacts with original technical manufacturing information, and co-using primary evidence from the plastic itself and historical industrial documentation. For this endeavor, I initiated an interdisciplinary collaboration between chemistry and conservation science, which led to the doctoral

study by chemist Robert Stewart (1997), jointly funded by the Engineering and Physical Sciences Research Council and the Scottish Conservation Bureau of Historic Scotland. This interdisciplinary research is the focus of my discussion.

Manufacturing chemists of the early 20th century talked about stability issues of plastics. A critical step for end-product quality was the removal of trace sulfuric acid and sulfates following the reaction between cellulose and a nitric acid mixture with sulfuric acid to facilitate the nitration. Inadequate washing at this stage resulted in a poor quality plastic. This once-common knowledge had been lost and forgotten with the demise of the cellulose nitrate industry in the 1960s (Meikle, 1995, p. 28) and overlooked by conservation scientists trying to understand the behavior of the historical material. Rediscovering the impact of residual sulfuric acid helped focus our attention on inherent manufacturing problems that explained the odd behavior of the historical plastic. It also transpired that past manufacturers viewed high levels of residual sulfate content as indicative of a poorly made product. Thus historical plastic with a detrimental acidic content was primary material culture evidence of quality control in the earliest of the man-made plastics. This casts a different light and novel value on degraded plastics in heritage collections, as windows into past industrial processes.

- *Bench Making of Cellulose Nitrates*

To understand the relevance of production quality and its relationship to the stability of historical cellulose nitrate plastic, we first need to understand its making. Manufacture operated within material boundaries imposed by the raw materials, the level of control over the chemical process, and the skill of the maker. All three had a physical impact on the material in terms of its mechanical and chemical durability and stability. This resonated in the shaky start of the first commercial production of cellulose nitrate plastic by Alexander Parkes in London in 1866 under the name of Parkesine. By 1868 Parkesine production had ceased because of poor quality resulting from cost-cutting measures to produce too much plastic with cheap materials (Friedel, 1983, p. 10). Customers complained that it distorted within a few weeks (Mossman, 1994, p. 15). When John Wesley Hyatt and his brother Isaac Smith started making their version, called Celluloid, in 1872 in the United States of America, they used camphor as a plasticizer and ethyl alcohol as the solvent. These were two ingredients that Parkes included in his 1865 patent for Parkesine, but deemed unnecessary to use himself until working for Daniel Spill in London to make Spill's version, called Xylonite, in the early 1870s (Friedel, 1983 p. 10-12).

Celluloid, Xylonite and other commercial brands of cellulose nitrate were more stable than Parkesine, and went on to commercial success as simulants of ivory, pearl, coral, jet, marble, tortoiseshell, amber, horn and onyx as well as in transparent form. The consumer market was favored by the dependable supply of the plastic compared to the natural materials (Friedel, 1983, p. 64). Cellulose nitrate plastic was produced in Europe and in the USA until the 1960s, and made into a wide range of household goods, decorative items, and industrial parts. The versatility of cellulose nitrate in sheet, extruded rod, and molded forms led to a broad and diverse range of applications over its production lifetime, including Victorian hair combs, Constructivist art sculptures in the 1920s, parts for planes and cars, pearlescent casings and finishes for accordions and other musical instruments, ammunition casings, and table tennis balls (Katz, 1985; Meikle, 1995). Additionally, there were cellulose nitrate films, lacquers, explosives, and, for a short time, fibers. It is little wonder, then, that cellulose nitrate has made its way into so many public museums, galleries, archives and historic houses, and private collections (Lavédrine *et al.*, 2012).

At its simplest constituent level, cellulose nitrate plastic is a polymer, which gives physical structure to the material, mixed with a plasticizer, which imparts flexibility. It was classed as a semi-synthetic because the polymer was made of cellulose from cotton and wood that was chemically modified by a nitrating acid mixture. Cellulose is composed of long chain molecules of carbon and hydrogen atoms with many hydroxyl (-OH) side groups, and it is these hydroxyls that are replaced with nitrate groups by an esterification reaction involving an aqueous acidic mixture of nitric acid, water and, importantly, sulfuric acid. With different formulations of the acid mixture, different degrees of nitration substitution of the cellulose hydroxyls were possible. The nitrogen content determined the physical properties of end-product: 10.5% for moldable plastics; 11.5% for films; and up to 13.5% for explosives (Boschan *et al.*, 1955; Reilly, 1991).

- *Manufacturing Problems*

Sulfuric acid played an essential controlling role in the first stage of the polymer-modification reaction pathway by forming cellulose sulfate esters, which were then substituted with nitrates. The right strength and proportion of sulfuric acid in the acid mix was crucial for regulating the substitution rate and number of nitrate molecules, which impacted on the nitration content and hence the end-product. Reaction conditions and quality of the starting materials influenced side-reactions, which also affected the end-result. The reaction solution was always a complex mix of cellulose, nitric acid, sulfuric acid, water, cellulose sulfates, cellulose nitrates, sulfonic

and nitrosulfonic acid esters, oxycellulose and hydrocellulose (Worden, 1911).

A well-documented stabilizing step was repeated post-reaction washing of the esterified cellulose to remove unwanted traces of sulfuric acid and sulfate esters. From the earliest days of Hyatts' process and throughout the production decades of cellulose nitrate, this removal of acidic residues was a critical stage (Friedel, 1983, p. 17). It was alerted to in many publications, including key works on cellulose esters by the American chemist Edward Chauncery Worden (1911, p. 595-596), publications by industrial chemists, like Foster Sproxton (1938), manager of the British Xylonite Company, and many others well into the 1950s (Miles, 1955). All noted that the quality of the end plastic depended on effective washing. The reason was that residual sulfuric acid would attack the structure-giving cellulose polymer backbone of the plastic, while the sulfate esters could form free acids, which catalyzed the degradation if not removed. Washing was done in large heated vats with boiling water until the overall acidity was reduced to 0.2% sulfate content or less (Worden, 1911). This proved to be a critical factor for the degradation susceptibility of historical cellulose nitrate.

Unstable cellulose nitrate plastic was always a concern of the manufacturers, and deemed a sign of a poor quality product. Problems included warping and distortion (Meikle, 1995, p. 23), and a yellow or brown color forming during 'seasoning' after processing or upon long storage (Worden, 1911). In the late 1920s, Ellington, a polymer chemist, investigated the problem with chemical analysis of fourteen transparent cellulose nitrate sheets manufactured in Germany, France, Britain, America, Switzerland and Japan which had yellowed and degraded (Ellington, 1929). His study showed that the two key destabilizing factors were the percentage (%) content of sulfate and of cellulose sulfate. The stable plastics had less than 0.1% total sulfate content whereas the unstable ones had 0.80% to 0.99% free sulfate and 0.24% to 0.63% cellulose sulfate. This chimes well with Stewart's modern analysis by ion chromatography of degraded historical cellulose nitrate plastic objects with varying visual signs of active degradation, such as discoloration, cracks, and characteristic square pattern crazing (Quye & Williamson, 1999, p.122-135; Shashoua, 2009, p. 151-184). The deteriorated aged plastics studied by Stewart all had a minimum of 0.5% total sulfate content. This was remarkably close to the 0.2% threshold maximum for a good quality plastic advocated by Worden a century earlier, demonstrating that manufacturers had the analytical capability and chemical understanding to measure and monitor the residual acid content of cellulose nitrate from the start of the 20th century, if not earlier. Indeed, they

acknowledged the importance of bench chemistry to control the properties of brand materials.

- *Opaque versus Transparent Plastic: A Clear Question of Quality*

Besides residual acids in degraded historical cellulose nitrate plastic, Stewart investigated another significant chemical composition factor linked to the common observation by conservators and curators - that transparent forms of the plastic tend to be more degraded than opaque forms. Again using ion chromatography, he found a high correlation between clear artifacts with visible cracks or yellowing and more than 0.5% sulfate content. However, if the plastic was opaque there were few visual signs of active degradation even if it was over the critical 0.5% total sulfate threshold. Why was this? Was there another quality relationship? The answer lay once again in the manufacturing chemistry for the plastic.

A lucrative consumer market for cellulose nitrate plastic was as a simulacrum of luxury natural materials. Imitation ivory, jet, pearl, coral and amber were popular forms (Böckmann, 1907, p. 97-100; Worden, 1911, p. 687-697), and it is under these guises that the plastic is often present in heritage collections or fashion, art, technology, social, and even natural history. To make imitation ivory and other opaque forms, the manufacturers added zinc oxide, zinc carbonate, or calcium carbonate to the cellulose nitrate dough (Sachs & Byron, 1921). Worden commented that "Transparent plastic is harder to keep stable than translucent and opaque, due to the stabilizing action of the zinc oxide and carbonate and other pigments present in the latter, and usually in large quantities" (Worden, 1911, p. 595).

Stewart readily detected zinc in historical samples of 'ivory' cellulose nitrate using X-ray fluorescence spectroscopy, and titanium from titanium dioxide, which was a common opacifier in many industrial applications from 1916. Stewart's sulfate analysis of these same artifacts confirmed that the minerals had maintained a protective effect over the decades in the plastics with over 0.5% of the detrimental sulfate content because they showed no sign of degradation. The chemicals added during manufacture to opacify the plastic were having a stabilizing effect on historical cellulose nitrate.

Cellulose nitrate manufacturers referred to their stabilizing chemical additives as antacids. Tellingly, the antacids were a safeguard against residual sulfuric acid and sulfates, and sometimes added even if deemed unnecessary at the time of production. The opacifying inorganic mineral were also classed as antacids, so their dual role as stabilizers was known. Antacids for transparent plastics were organic compounds, like urea (Worden, 1911). There were differing opinions about whether antacids for transparent cellu-

lose nitrate covered up a poorly-manufactured product. Antacids were encouraged in a book about European cellulose nitrate production in the 1910s (Masselon *et al.*, 1912) while a book about the American cellulose nitrate industry, published at the same time, endorsed thorough washing and advised against antacids (Worden, 1911). Washing was the industry-wide preference on both sides of the Atlantic. In Ellington's research of the different makes of cellulose nitrate sheet (Ellington, 1929), he classed the stable plastics with low sulfate content and little urea or mineral content as high quality, viewing the low sulfate levels as good production control. Samples with high quantities of sulfate contained appreciable levels of urea (0.2% to 1.2%), which Ellington deemed "objectionable" to him as a polymer chemist. He referred to the urea as "artificial stabilisation" because manufacturers would have been aware that the sulfate in their material was an "undesirable impurity". Studies of urea in historical cellulose nitrate plastics have not been published yet, but urea content should be investigated to see if it is detectable and correlates with the stability of the historical plastics.

Herein lies an interesting quality question with implications for the interpretation of historical collections. If it took better production control to make a stable transparent cellulose nitrate than it did for an opaque form because the opacifying minerals acted as antacids, were lower quality plastics used to make the expensive-looking simulants like ivory, pearl, coral and onyx? If so, the technological value and quality of clear cellulose nitrates would be higher than the simulants despite the simulants having more aesthetic appeal and looking like a better class of material. Of course not all clear cellulose nitrate plastics were necessarily high quality, as evidenced by the many instances of degraded historical drawing instruments which tend to be transparent, but it does open up a new area for discussion about intrinsic and implied material value of historical synthetic simulants of natural materials between historians and curators of design and technology.

Chemistry Matters

While Stewart's analytical study of degraded cellulose nitrate plastic links long-term stability to residual acids and added opacifiers from manufacture, it is only a partial insight into the chemical complexities of the end-product. Making cellulose nitrate was a multi-stage chemical balancing act. With the industry spanning from the 1860s to the early 1960s, it covered a monumental period of increasing chemical understanding as well as technical and social change. Manufacturing transitioned from an arena of exper-

imentation and trade secrets to targeted research and greatly enhanced chemical knowledge of the materials and product. Yet the basic chemistry of the process did not change. What impact did this have on the material quality? And what are the implications for historical collections? Do the longevity and stability of old cellulose nitrate plastics correlate with date of production? To begin finding answers, the role of chemistry in the industry needs to be examined more closely.

Chemistry was intrinsic throughout the whole process of making cellulose nitrate. From its earliest days, the cellulose nitrate industry acknowledged the necessary input of chemists. Raw materials, solvents and additives had to be selected, purity-tested and prepared. The nitrating acid mixture needed specific formulations, while the esterification step required monitoring and control. Spent acid had to be removed and recycled. The right type and amount of solvent and plasticizer had to be added to the nitrated cellulose to make a 'colloidon' of the required viscosity for handling and shaping. Chemists were employed as in-house analysts and managers to select the best materials and to control the process. This included solvent solubility tests for the degree of cellulose nitration, and viscosity measurements to assess physical quality for processing (Schüpphaus, 1915; Partidge, 1929). Hyatt said he was "allowed to employ a chemist [Mr Frank Vanderpoel] for determining our acids and to systemize our nitration, instead of merely using hydrometers and thermometers" (Hyatt, 1914).

The era between the 1870s and early 1900s was one of empirical venture for the makers, but driven more by tacit technical experience and commercial enterprise rather than systematic scientific advances (Friedel, 1983). The molecular structure of cellulose was not deduced by Cross, Bevan and Beadle until 1895, although as it turned out advancements in polymer and macromolecular theories over the following decades had little effect on improving the quality of manufactured cellulose nitrate plastic. The best raw materials and additives were found early on because of industrial trials and observations (Friedel, 1983). This included a good plasticizer to soften the nitrocellulose polymer for shaping and molding, and a good solvent (Ott, 1940; Friedel 1983). The Hyatts and Daniel Spill used camphor, a natural extract from the wood and bark of the Japanese *Formosa* tree, as a plasticizer from the outset for their cellulose nitrate plastics in the 1870s. The undesirable pungency of camphor and its cost at the turn of the 20th century led to the testing of no less than 44 chemicals and many derivatives as substitutes (DuBois, 1907, p. 40-41), while oil of turpentine was used in World War I because of camphor supply shortages (Mork, 1917). Other alternatives were also trialed periodically (Sachs & Byron, 1921; Durans & Davidson, 1936), but camphor remained the best choice. Hyatt also

decided on ethyl alcohol for the solvent and patented the important process of 'seasoning' the finished product to allow all solvent traces to evaporate for stabilization (Meikle, 1995).

With good choices of camphor plasticizer and ethyl alcohol solvent from the outset, and awareness of residual acids and the benefits of antacid stabilizers in place by the start of the 20th century, the industry had established in its early days what chemists at that time considered to be the four strong pillars of material stability for the plastic. The main advance for the cellulose nitrate plastic manufacture in the 20th century was not so much the chemistry of the material, but rather controlling the many variables mentioned above during the production stages. Old industrial processes were revisited and re-evaluated (Lunge, 1901), advancements made in cellulose chemistry (Briggs, 1915), and the benefits of systematic applied chemistry advocated to help solve industrial problems (Bacon & Hamor, 1919). In 1920, Staudinger's macromolecular theory classified plastics as polymers. The crystalline structure of cellulose was revealed by X-rays one decade later (Clark, 1930). By the end of the 1920s it was agreed that cellulose was a polymeric chain of cellobiose monomers (Badgley *et al.*, 1945), but the direct impact of these major theoretical chemistry advances on cellulose nitrate plastic quality was far less than might be expected. The chemical process approach to esterification had changed very little since the beginning (Yarsley *et al.*, 1964, p. 173). Instead, the developments were more advantageous to manufacturing processes for the new related plastics made from cellulose acetate and other cellulose derivatives.

By the 1920s interest was growing in colloid chemistry to measure and characterize the viscosity of colloidon (Bancroft, 1922). This was driven further in the 1930s by the advent of fiber extrusion and injection-molding for cellulose acetate, although this did not benefit cellulose nitrate plastic much because these mechanical processes did not suit its flammable tendencies. The advent of the ultracentrifuge in 1938 improved viscosity measurements for cellulose nitrate plastics (Kraemer, 1938). However, the chemical complexity and control over minute changes throughout the whole process of making cellulose nitrate could not be overcome with the extent of knowledge about colloid chemistry at that time (Conaway, 1938). By the time polymer chemistry had matured in the 1940s, it was of more value to the expanding fiber-making industries for filament extrusion of viscose rayon and cellulose acetate, and for tailor-making cellulose derivatives rather than improving cellulose nitrate plastics (Tinsley, 1948). The rise of the more controllable petrochemical plastics proved too much competition for the variances of cellulose nitrate (Meikle, 1995, p. 23). Cellulose nitrate plastic was by now less appealing because its preparation was so sen-

sitive, with even small changes in the equilibrium having unpredictable effects (Conaway, 1938).

Despite a steady increase in chemical research for commercial cellulose nitrate manufacture from the 1910s to the 1930s, with a move from small factory works to scientific institutions and industrial labs (Morris, 2015, p. 242-252), plus commercial and academic investment in research, practical issues of variable chemical reaction parameters for cellulose nitrate plastic could not be resolved. Eventually commercial manufacture started declining in America in the mid-1950s amid competition from other better-controlled synthetic plastics (Meikle, 1995, p. 28). In 1963, the few European companies still making cellulose nitrate plastic were using old equipment, while Japanese manufacturers used advanced technology (Kaufman, 1963). By this date, cellulose nitrate was no longer produced in the USA, but was still available and continued to be used for brush handles and spectacle frames (Yarsley *et al.*, 1964).

What does this overview of past cellulose nitrate plastic manufacture offer to the conservation science of cellulose nitrate plastics? The upshot is that despite progressive chemical understanding and a rise in research investment, there were surprisingly few major chemical step-changes for the manufactured material. With regards to the common heritage science application of material analysis to provenance the origin or date of an historical object, the chemical composition of commercial cellulose nitrate plastic can only enlighten us a little. The presence of a titanium opacifier would indicate a date post-1916 and, with more research, camphor substitutes used by different manufacturers, for example oil of turpentine derivatives, could be linked to specific periods. Other factors like the design and style of the object and trademarks would be more informative. Nonetheless, material information is still important to collect for preservation needs. For example, oil of turpentine derivatives discolored imitation ivory (Sachs & Byron, 1921), so its presence in an aged object would predict or explain changes to its appearance.

Gaining better appreciation of the quality challenges that the historical commercial makers faced to control vagaries in the process makes the random degradation between similarly dated or produced objects more understandable. It is an inherent vice, yet this does not detract from the benefits of analyzing degraded objects materials with well-known provenance, instead enhancing further the material picture of production quality effects and connecting material evidence to past written observations and tests.

Changing Values of Brand Materials

The correlation between the chemical composition of artifacts and their physical condition by Stewart was made possible by the direct analysis of various artifacts, from good to poor quality. This invaluable primary source research relied on collectors and curators appreciating that, in this instance, de-accessioning and sacrificing a small number of historical objects would answer greater questions about stability to the benefit of many more in heritage collections. Some de-accessioning decisions were justified on the grounds that material breakdown had reached a critical point such that the artifact no longer had significance or value in the context of the collection and was also putting other parts of the collection at risk from the emissions of its degradation products.

In this way, these historical materials inadvertently acquired a new value for industrial heritage. While on one hand the degradation of material culture can result in irretrievable or irreversible loss of the form or function of artifacts, on the other these collections of historical materials enter a new phase of historical value, becoming “monuments of history” as material culture objects that reveal history and passage of time (Muñoz Viñas, 2005). Thus, un-degraded and degraded historical cellulose nitrate plastics both come to share significance and a material culture value for the conservation scientist and industrial historian, where there are mutual interests in product, production and quality. From its primary use as a brand material to one as an historical object in a heritage collection, an artifact experiences its first shift of significance. When it is removed from a collection because of degradation, the same artifact acquires a second and new value, as an invaluable material for experimental conservation science research into the processes of aging and deterioration.

Especially valuable for direct primary source evidence from the past are materials with well-documented provenance: where, when, and how they were made. For conservation scientists, company archives of products and production records provide significant historical clues. Detailed information is also essential for reconstructions of historical processes as another invaluable resource for technical history research (Staubermann, 2009). It is as important to preserve and understand not just the manufactured end-product but the raw materials and the manufacturing processes, and to preserve manufacturers' samples and associated knowledge through business archives. Increasing digitization allows on-line access to publications from the late 19th century and early to mid-20th century, such as *Industrial and Engineering Chemistry*, where much was published about the early plastics industry that now documents its growth and changes. Access to these publications has significantly aided and enhanced research to connect artifacts

and modern production for conservation science, revealing an abundance of information from other chemical industries, such as the related synthetic fibers (Quye, 2014) and synthetic dyes (Quye, 2016). Likewise, it is essential to preserve the physical evidence of the products and documentation of production, and for conservation understanding to grow about materials for informed “interventive conservation”¹ (Shashoua, 2016), and for collection management of artifacts and archives (Brokerhof & Bülow, 2016). Uniting industry and historical material culture in this way offers a potent reconnection between maker and product.

Conclusion: From the Preservation of Materials to Interdisciplinary Research

While there is an obvious desire to keep old cellulose nitrate plastics ‘alive’ so that their function, form and aesthetic can be appreciated and understood, their ‘death’ brings an unexpected insight into their material composition and manufacture, with the process and products of degradation providing invaluable pieces of primary chemical evidence of past production. Within the degraded plastic itself is a direct connection between material stability, the chemistry of the manufacturing process, and quality control during manufacture. Linking the chemical evidence in degraded and un-degraded cellulose nitrate historical artifacts with contemporaneous scientific accounts of their manufacture from those who understood the scientific principles of manufacture brings those historians interested in 19th century and early 20th century chemical manufacturing closer to direct primary evidence of quality control.

This a tale to emphasize that preservation of material culture makes knowing and understanding industrial techniques valuable and necessary. As observers with the gift of hindsight, we witness in cellulose nitrate plastic a threshold amount of a known malignant acidic residue that was just acceptable when made but has now become a destabilizing inherent vice with time. That there was a need to rediscover a well-known phenomenon first reported over a century ago and common knowledge until just 60 years ago says much about how easily and quickly information is lost with the decline of a commercial manufacturing industry. Research like Stewart’s reconnects the material evidence in the historical object with past manufacturing method information, and revives the understanding to recognize the

¹ “Interventive conservation” deals with the physical treatment of objects, like cleaning or repair, whereas “passive conservation” seeks to control environmental conditions such as temperature and humidity.

significance of objects and their contextual information. In this case, a quality issue inherent in a past manufactured product has resurfaced as a consequence of the material being kept by museums and collectors for longer than the manufacturers could have expected.

Researching historical materials for conservation science entails three essential aspects for meaningful and progressive insight: interdisciplinary collaborations; access to digitized, searchable archives; and an understanding of the chemistry of materials. The research described in this chapter for cellulose nitrate would not have been successful without cooperative understanding between an analytical scientist, a polymer chemist, and a conservation scientist. Our multidisciplinary discussions gave insight into the past industrial production of a material and connected the research to the history of science. In short, the breakdown of an inanimate material brought a new community of people together in a dialogue where chemistry, conservation and history had to be articulated and interconnected.

The study presented is by no means a unique example of how preservation brings insight to past technology and production quality. Collaborative research between conservation scientists at the Kunst Historische in Vienna and historians revealed that the unexpected and unlikely corrosion of gold coins minted in the 19th century related to the dies carrying traces of contamination iron from other coins onto the surface of the gold coin (Traum & Griesser, 2006). Taking a look beyond what is happening to the aged material now and placing its present chemical condition in the context of its production takes historical materials research beyond issues of current preservation state into the realms of technical production and industrial quality.

The multidisciplinary collaboration of material chemists and heritage scientists, and knowledge exchange with curators and historians of technology and industry is enlivening, indeed vital, when the maker's voice is lost. Access to historical manufacturing information greatly assists conservation scientists and conservators in their quest to understand more about original modern industrial materials. At this point in time there are many examples of historical cellulose nitrate, but with loss through degradation, preservation of these once common mass-produced objects becomes even more pressing especially if other sources of related information disappear (Muñoz Viñas, 2005).

While any loss of material culture is lamentable to its collector and custodian, especially when the object loses significance because it is no longer physically intact nor accessible in its broadest sense, or becomes a health hazard or is detrimental to other artifacts, it can attain a new role within historical and socioeconomic frameworks. An historical object trav-

els different paths in its journey through the material culture world where it will be judged by our changing perspectives on value and significance. It may seem that the end of its useful 'life' will be the day when the object loses its material coherence and physically breaks down. To the materials scientist, this point can be the start of a new journey of discovery. Even if an object can no longer be used or understood, like the spectacles in Figure 1, its degraded material composition is a bridge to an otherwise distanced world of its creation.

In the context of stabilization of cellulose nitrate plastics, the endeavors of the industrial chemists testing the quality of the material for the consumer lifetime of the material are similar to the conservation scientists' testing of the composition of aged material to extend the artifact's lifetime. The connections among chemists, polymer scientists, engineers, and industrialists in the historical production of brand plastics is mirrored in the knowledge exchange community of chemists, conservation scientists, conservators, historians, and curators for the promotion and conservation of material collections. When quality matters for industrial heritage, historical objects benefit from new conversations in history of science for material significance and preservation.

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